PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-092436
(43)Date of publication of application : 10.04.1998

(51)Int.Cl. H01M 4/62
H01M 4/02
H01M 4/58
H01M 10/40

(21)Application number : 08-265408
(22)Date of filing : 13.09.1996

(71)Applicant : SANYO ELECTRIC CO LTD
(72)Inventor : SHOJI YOSHIHIRO
KUSUMOTO YASUYUKI
YAMAZAKI MIKIYA
NOMA TOSHIYUKI
NISHIO KOJI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To enhance the wettability of a negative electrode against nonaqueous electrolyte so as to obtain superior high rate discharge characteristics by providing the negative electrode made by forming a carbon layer containing a nonionic surfactant on the surface of a collector.
SOLUTION: A negative electrode is made by forming a carbon layer containing a nonionic surfactant which can electrochemically store and discharge negative electrode active material ions on the surface of a collector. Preferably, the nonionic surfactant content of the carbon layer is 0.5 to 5 percentage by weight. When the content is less than 0.5 percentage by weight, a wettability improving effect is not sufficient, and when the content exceeds 5 percentage by weight, the adhesion of the carbon layer and the collector is deteriorated so that high rate discharge characteristics are deteriorated. Thereby, the wettability of the negative electrode against nonaqueous electrolyte is excellent so that the effective area of electrode reaction is large, and discharge capacity of high load discharge becomes large so as to obtain the superior high rate discharge characteristics.

CLAIMS

[Claim(s)]
[Claim 1]A nonaqueous electrolyte secondary battery, wherein said carbon layer contains a nonionic surface active agent in a nonaqueous electrolyte secondary battery provided with a negative electrode which forms electrochemically occlusion and a carbon layer which can be emitted on the surface of a charge collector for negative-electrode-active-material ion.
[Claim 2]The nonaqueous electrolyte secondary battery according to claim 1 in which said nonionic surface active agent is polyoxyethylene alkyl ether, polyoxy alkylphenyl ether, polyoxyethylene poly styryl phenyl ether, or polyoxyethylene polyoxypropylene glycol.
[Claim 3]The nonaqueous electrolyte secondary battery according to claim 1 or 2 with which said carbon layer contains a nonionic surface active agent 0.5 to 5% of the weight.
[Claim 4]A nonaqueous electrolyte secondary battery, wherein said carbon body contains a nonionic surface active agent in a nonaqueous electrolyte secondary battery provided with a negative electrode which joins a carbon body which binds electrochemically occlusion and the end of carbon powder which can be emitted for negative-electrode-active-material ion to a charge collector.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which an invention belongs] The negative electrode in which this invention forms electrochemically occlusion and the carbon layer which can be emitted on the surface of a charge collector for negative-electrode-active-material ion, Or with respect to a nonaqueous electrolyte secondary battery provided with the negative electrode which consists negative-electrode-active-material ion of a carbon body which binds electrochemically occlusion and the end of carbon powder which can be emitted, and a charge collector, it is related with improvement of the negative electrode aiming at improving the high rate discharging characteristic in detail.
[0002]
[Description of the Prior Art]In recent years, carbon materials, such as occlusion and corks which can be emitted, and black lead, attract attention electrochemically in active material ion, such as a lithium ion, as a negative pole material of a nonaqueous electrolyte secondary battery from the Reasons of excelling in the reversibility at the time of charge and discharge.
[0003]The negative electrode using a carbon material applies the slurry containing a binder and a thickener to a charge collector, and is dried in the end of carbon powder, forming a carbon layer on the surface of a charge collector (for example, negative electrode of a cylindrical cell) -- or it is produced by joining the pressing object of the mixture of the end of carbon powder, and a binder to a charge collector (for example, negative electrode of a flat type battery). For example, the negative electrode which applied the coating liquid (slurry) containing styrene / butadiene latex (binder), and carboxymethyl cellulose (thickener) to nickel foil (charge collector), and was produced by drying is indicated by JP,H5-74461,A in the end of carbon powder.
[0004]However, the wettability to nonaqueous electrolyte originates in it not being good, and there is SUBJECT that a high rate discharging characteristic is not good in the negative electrode using a carbon material.
[0005]This invention is made in order to solve this SUBJECT, and an object of this invention is for the wettability to the nonaqueous electrolyte of a negative electrode to provide the good

nonaqueous electrolyte secondary battery excellent in the high rate discharging characteristic.

[0006]

[Means for Solving the Problem]In a nonaqueous electrolyte secondary battery provided with a negative electrode which forms electrochemically occlusion and a carbon layer which can be emitted on the surface of a charge collector for negative-electrode-active-material ion, as for a nonaqueous electrolyte secondary battery concerning the invention according to claim 1, said carbon layer contains a nonionic surface active agent.

[0007]A nonaqueous electrolyte secondary battery concerning the invention according to claim 4, In a nonaqueous electrolyte secondary battery provided with a negative electrode which joins a carbon body which binds electrochemically occlusion and the end of carbon powder which can be emitted for negative-electrode-active-material ion to a charge collector, said carbon body contains a nonionic surface active agent. In this Description, a nonaqueous electrolyte secondary battery concerning the invention according to claim 1 and a nonaqueous electrolyte secondary battery concerning the invention according to claim 4 may be named this invention cell generically.

[0008]A surface-active agent a carbon layer or a carbon body is made to contain is limited to a nonionic surface active agent because service capacity will decrease, if a surface-active agent of ionicity is used. This is imagined to be what is depended on the following Reason. That is, in a nonaqueous electrolyte secondary battery which uses a carbon material for a negative electrode, since it is a discharge state when a cell is produced, in order to make it discharge, it is necessary to charge. With a carbon negative electrode, an irreversible reaction occurs an appropriate place at the time of this charge. Since this irreversible reaction is promoted when a surface-active agent of ionicity is used, it is thought that service capacity decreases.

[0009]As an example of a nonionic surface active agent, polyoxyethylene alkyl ether, polyoxy alkylphenyl ether, polyoxyethylene poly styryl phenyl ether, and polyoxyethylene polyoxypropylene glycol are mentioned. These nonionic surface active agents may be used by a kind independent, and may use two or more sorts together if needed.

[0010]As for a carbon layer or nonionic surface active agent content of a carbon body, 0.5 to 5 % of the weight is preferred. Since the wettable improvement effect is not enough when the content is less than 0.5 % of the weight, and since the binding property of comrades falls in the adhesion of a carbon layer and a charge collector, or the end of carbon powder when the content exceeds 5 % of the weight, a high rate discharging characteristic falls.

[0011]Since a negative electrode of this invention cell containing a nonionic surface active agent has good wettability to an electrolysis solution, its effective surface area of an electrode reaction is large. For this reason, this invention cell has large service capacity of high load discharging. That is, it excels in a high rate discharging characteristic. This invention is applied to a lithium secondary battery, for example, and is preferred.

[0012]

[Example]Although this invention is explained still in detail based on working example, in the range which is not limited to following working example at all, and does not change the gist, it changes suitably and this invention can be carried out.

[0013](Experiment 1) In this experiment, the quantity of the nonionic surface active agent at the time of using polyoxyethylene methyl ether as a nonionic surface active agent and the relation of the high rate discharging characteristic were investigated.

[0014][Production of an anode] Mixture 95 weight section of the weight ratio 9:1 of $LiCoO_2$ powder with a mean particle diameter of 5 micrometers and artificial-graphite powder, Knead the 5-% of the weight N-methyl-2-pyrrolidone solution of polyvinylidene fluoride 5 weight section, prepare a slurry, and this slurry is applied to both sides of aluminium foil with a doctor blade method, After forming the active material layer of 50-micrometer thickness in each field of foil, vacuum drying was carried out by 150 degreeC for 2 hours, and the anode was produced.

[0015][Production of a negative electrode] To the water dispersion of the natural-graphite-powder end of 20-micrometer mean particle diameter (98-X weight section; however X= 0, 0.25, 0.5, 1, 2, 3 and 4, or 5), and styrene-butadiene-rubber latex (solid content: one weight section). Addition mixing of polyoxyethylene methyl ether (X weight section) and the carboxymethyl cellulose solution (solid content: one weight section) was carried out, and the slurry was prepared. After applying this slurry to both sides of copper foil with the doctor blade method and forming the carbon layer of 50-micrometer thickness in each field of foil, vacuum drying was carried out by 150 degreeC for 2 hours, and the negative electrode was produced.

[0016][Preparation of nonaqueous electrolyte] In the mixed solvent of the volume ratio 2:3 of ethylene carbonate and diethyl carbonate, 1 mol/l. $LiPF_6$ was melted, and nonaqueous electrolyte was prepared to it.

[0017][Production of a cell] The lithium secondary battery A0 (X= 0) of AA size, A1 (X= 0.25), A2 (X= 0.5), A3 (X= 1), A4 (X= 2), A5 (X= 3), A6 (X= 4), and A7 (X= 5) were produced using an above-mentioned anode, negative electrode, and nonaqueous electrolyte. The fine porous membrane made from polypropylene was used for the separator.

[0018]<Charge and discharge test> After charging each cell to 4.1V by 1C by 25 degreeC, it discharged to 2.75V by 1C and 2C, and asked for the ratio (%) of the service capacity in 2C to the service capacity in 1C. A result is shown in drawing 1.

[0019]this invention cells A1-A7 have a ratio of the service capacity in 2C to the service capacity in 1C higher than drawing 1 compared with the comparison cell A0, and it turns out that it excels in the high rate discharging characteristic. Since this invention cells A2-A7 are excellent in especially the high rate discharging characteristic also in this invention cells A1-A7, the polyoxyethylene methyl ether content of a carbon layer is understood that 0.5 to 5 % of the weight is preferred.

[0020](Experiment 2) In this experiment, the quantity of the nonionic surface active agent at the time of using polyoxy methylphenyl ether as a nonionic surface active agent and the relation of the high rate discharging characteristic were investigated. It is in the experiment 1 except having replaced with polyoxyethylene methyl ether and having used polyoxy methylphenyl ether.

[Production of a cell] Similarly The lithium secondary battery B1 (X= 0.25), B-2 (X= 0.5), B3 (X= 1), B4 (X= 2), B5 (X= 3), B6 (X= 4), and B7 (X= 5) were produced, the charge and discharge test of the conditions same about each cell as the point was done, and it asked for the ratio of the service

capacity in 2C to the service capacity in 1C. A result is shown in drawing 2. The result of the lithium secondary battery A0 produced in the experiment 1 is also posted and shown in drawing 2 from drawing 1.

[0021]this invention cells B1-B7 have a ratio of the service capacity in 2C to the service capacity in 1C higher than drawing 2 compared with the comparison cell A0, and it turns out that it excels in the high rate discharging characteristic. Since this invention cell B-2 - B7 are excellent in especially the high rate discharging characteristic also in this invention cells B1-B7, the polyoxy methylphenyl ether content of a carbon layer is understood that 0.5 to 5 % of the weight is preferred.

[0022](Experiment 3) In this experiment, the quantity of the nonionic surface active agent at the time of using polyoxyethylene poly styryl phenyl ether as a nonionic surface active agent and the relation of the high rate discharging characteristic were investigated. It is in the experiment 1 except having replaced with polyoxyethylene methyl ether and having used polyoxyethylene poly styryl phenyl ether. [Production of a cell] The lithium secondary battery C1 (X= 0.25), C2 (X= 0.5), similarly, C3 (X= 1), C4 (X= 2), C5 (X= 3), C6 (X= 4), and C7 (X= 5) were produced, the charge and discharge test of the conditions same about each cell as the point was done, and it asked for the ratio of the service capacity in 2C to the service capacity in 1C. A result is shown in drawing 3. The result of the lithium secondary battery A0 produced in the experiment 1 is also posted and shown in drawing 3 from drawing 1.

[0023]this invention cells C1-C7 have a ratio of the service capacity in 2C to the service capacity in 1C higher than drawing 3 compared with the comparison cell A0, and it turns out that it excels in the high rate discharging characteristic. Since this invention cells C2-C7 are excellent in especially the high rate discharging characteristic also in this invention cells C1-C7, the polyoxyethylene poly styryl phenyl ether content of a carbon layer is understood that 0.5 to 5 % of the weight is preferred.

[0024](Experiment 4) In this experiment, the quantity of the nonionic surface active agent at the time of using polyoxyethylene polyoxypropylene glycol as a nonionic surface active agent and the relation of the high rate discharging characteristic were investigated. That is, it is in the experiment 1 except having replaced with polyoxyethylene methyl ether and having used polyoxyethylene polyoxypropylene glycol. [Production of a cell] The lithium secondary battery D1 (X= 0.25), D2 (X= 0.5), similarly, D3 (X= 1), D4 (X= 2), D5 (X= 3), D6 (X= 4), and D7 (X= 5) were produced, the charge and discharge test of the conditions same about each cell as the point was done, and it asked for the ratio of the service capacity in 2C to the service capacity in 1C. A result is shown in drawing 4. The result of the lithium secondary battery A0 produced in the experiment 1 is also posted and shown in drawing 4 from drawing 1.

[0025]this invention cells D1-D7 have a ratio of the service capacity in 2C to the service capacity in 1C higher than drawing 4 compared with the comparison cell A0, and it turns out that it excels in the high rate discharging characteristic. Since this invention cells D2-D7 are excellent in especially the high rate discharging characteristic also in this invention cells D1-D7, the polyoxyethylene polyoxypropylene glycol content of a carbon layer is understood that 0.5 to 5 % of the weight is preferred.

[0026](Experiment 5) This experiment considered the relation between the kind of surface-active agent, and the service capacity of a negative electrode the carbon layer of a negative electrode is made to contain.

[0027][Production of a test electrode] In the natural-graphite-powder end of 20-micrometer mean particle diameter to the water dispersion of 96 weight sections and styrene-butadiene-rubber latex (solid content: one weight section). Polyoxyethylene methyl ether (nonionic surface active agent), methylbenzene sulfone sodium (anionic surfactant), Addition mixing of methylammonium chloride (cationic surfactant) or N-methylamino acid (ampholytic surface active agent) (the amount part of duplexs), and the carboxymethyl cellulose solution (solid content: one weight section) was carried out, and the slurry was prepared. These slurries are applied to both sides of copper foil with a doctor blade method, After forming the carbon layer of 50-micrometer thickness in each field of foil, vacuum drying is carried out by 150 degreeC for 2 hours, The test electrode E1 (surface-active agent: polyoxyethylene methyl ether), E2 (surface-active agent: methylbenzene sulfone sodium), E3 (surface-active agent: methylammonium chloride), and E4 (surface-active agent: N-methylamino acid) were produced.

[0028][Production of a test cell] Each above-mentioned test electrode (working pole) and metal lithium foil (counter electrode) were spirally rolled via the fine porous membrane made from polyethylene (separator), and the electrode body was produced. This electrode body was stored in the cell which put in nonaqueous electrolyte with the metal lithium board (reference pole), and the test cell was produced. As nonaqueous electrolyte, the same thing as what was used in the experiments 1-4 was used.

[0029][Charge and discharge test] After charging each test cell to 0V (vs.Li/Li^+) by current density 0.1 mA/cm^2 by 25 degreeC, it discharged to 1V (vs.Li/Li^+) by current density 0.1 mA/cm^2, and service capacity was calculated. A result is shown in Table 1.

[0030](Reference experiment) This reference experiment considered the relation between the kind of surface-active agent at the time of adding a surface-active agent to an anode, and the service capacity of an anode.

[0031][Production of a test electrode] Mixture 93 weight section of the weight ratio 9:1 of $LiCoO_2$ and an artificial graphite with a mean particle diameter of 5 micrometers, The 5-% of the weight N-methyl-2-pyrrolidone solution of polyvinylidene fluoride 5 weight section is kneaded, Furthermore, the amount part addition of duplexs was carried out, polyoxyethylene methyl ether, methylbenzene sulfone sodium, methylammonium chloride, or N-methylamino acid was kneaded, and the slurry was prepared. These slurries are applied to both sides of aluminium foil with a doctor blade method, After forming the active material layer of 50-micrometer thickness in each field of foil, vacuum drying is carried out by 150 degreeC for 2 hours, Test electrode F1 (surface-active agent: polyoxyethylene methyl ether), F2 (surface-active agent: methylbenzene sulfone sodium), F3 (surface-active agent: methylammonium chloride), and F4 (surface-active agent: N-methylamino acid) were produced.

[0032][Production of a test cell] Each above-mentioned test electrode (working pole) and metal

lithium foil (counter electrode) were spirally rolled via the fine porous membrane made from polyethylene (separator), and the electrode body was produced. This electrode body was stored in the cell which put in nonaqueous electrolyte with the metal lithium board (reference pole), and the test cell was produced. As nonaqueous electrolyte, the same thing as what was used in the experiments 1-4 was used.

[0033][Charge and discharge test] Each test cell was discharged to 2.75V (vs.Li/Li^{+}) by current density 0.1 mA/cm^2 in 25 degreeC, and service capacity was calculated. A result is shown in Table 1.

[0034]

[Table 1]

試験電極	界面活性剤	正極放電容量(mAh/g)	負極放電容量(mAh/g)
E 1	ポリオキシエチレンメチルエーテル	………	3 7 0
E 2	メチルベンゼンスルホン酸ナトリウム	………	2 5 0
E 3	メチルアンモニウムクロリド	………	2 3 0
E 4	N－メチルアミノ酸	………	2 0 0
F 1	ポリオキシエチレンメチルエーテル	1 3 0	………
F 2	メチルベンゼンスルホン酸ナトリウム	1 2 8	………
F 3	メチルアンモニウムクロリド	1 2 9	………
F 4	N－メチルアミノ酸	1 2 8	………

[0035]As shown in Table 1, the test electrode E1 has markedly large service capacity compared with the test electrode E2, E3, and E4. This fact shows that a nonionic surface active agent is preferred as a surface-active agent a carbon layer is made to contain for the improvement in wettable of a negative electrode. As shown in Table 1, in test electrode F1-F4, a significant difference is not observed in service capacity. This fact shows that the surface-active agent in particular an active material layer is made to contain for the improvement in wettable of an anode is not restricted unlike the case of a negative electrode.

[0036]Although the case where this invention was applied to a lithium secondary battery was mentioned as the example and above-mentioned working example explained it, this invention is widely applicable to a nonaqueous electrolyte secondary battery. Although the cylindrical cell was mentioned as the example and above-mentioned working example explained it, this invention is applicable to the cell of various shape, such as each [a flat type and] mold.

[0037]

[Effect of the Invention]Since this invention cell has the good wettability of a negative electrode to an electrolysis solution, it excels in a high rate discharging characteristic.

[Translation done.]